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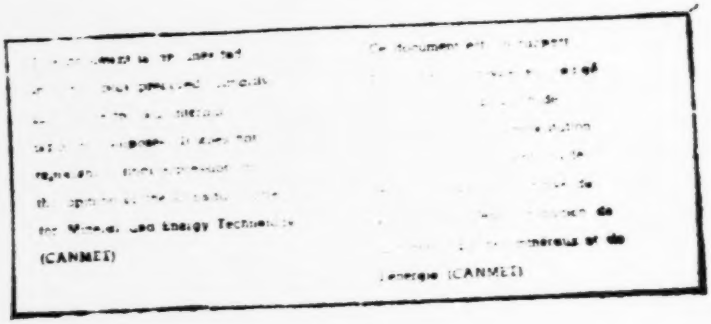
EFFECT OF V AND Cr ALLOY ADDITIONS ON THE STRUCTURE AND PROPERTIES OF A Nb LINE-PIPE STEEL

L.E. Collins, M.J. Godden and J.D. Boyd

Metallurgy Section



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ABSTRACT

The effects of Cr (0-0.31%) and V (0-0.11%) additions on the tensile and Charpy impact properties of a controlled-rolled Nb line-pipe steel were investigated. Continuous-cooling-transformation (CCT) diagrams were also developed to determine the effects of these alloy additions on the transformation behaviour of the steel. Only small increases in tensile and yield stress occurred with increasing V content, ≈28 MPa/0.1% V (4 ksi/0.1% V). Additions of Cr $\leq$0.15% had little effect on strength, but an increase was observed at 0.30 Cr. Neither V nor Cr changed the 20 J Charpy transition temperature and the shelf energy was dependent only on the S content of the steels. The CCT diagrams showed that the V and Cr additions used had very little effect on the ferrite and bainite transformation kinetics. Both Cr and V acted to suppress pearlite formation thus promoting the formation of bainite and martensite-retained austenite (M/A) from the carbon rich austenite present in the final stages of transformation. This effect was particularly strong in alloys containing both Cr and V.

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RÉSUMÉ

On a étudié les effets de l'addition de Cr (0-0,31%) et de V (0-0,11%) sur les propriétés de résistance à l'impact Charpy et de résilience en traction d'un acier Nb contrôlé et laminé, pour tuyaux de canalisation. On a également développé des diagrames de transformation et refroidissement continus (CCT; continuous-cooling-transformation) pour déterminer les effets de ces additions d'alliage sur le comportement de l'acier en transformation. Il n'y a eu que de légères augmentations de l'effort en traction et de la charge de la limite d'écoulement avec l'augmentation du contenu de V, ≈28 MPa/0,1% V (4 ksi/0,1% V). L'addition de Cr $\leq$0,15% a eu très peu d'effet sur la résistance alors qu'on a observé un accroissement de cette dernière à 0,30 Cr. Ni le V, ni le Cr n'ont changé la température de transition Charpy de 20 J, et le pallier énergétique ne dépendait que du contenu de S dans les aciers. Les diagrammes de CCT ont démontré que les additions de V et de Cr utilisées n'ont eu que très peu d'effet sur la cinétique de transformation de la bainite et la ferrite. Le Cr et le V ont supprimé tous deux la formation de perlite, favorisant ainsi la formation de bainite et d'austénite retenue par la martensite (M/A) à partir du charbon riche en austénite présent dans les dernières étapes de la transformation. Ces effets étaient particulièrement forts dans les alliages contenant à la fois du Cr et du V.

INTRODUCTION

Steels for line-pipe applications are designed to have high strength and toughness in combination with good weldability. The necessary fine-grained ferrite structures are obtained by means of controlled rolling and careful alloy additions. Controlled-rolling practice seeks to produce a fine deformed austenite (γ) structure which will transform to a fine ferrite (α) structure if the $\gamma - \alpha$ transformation can be suppressed to a sufficiently low temperature. The development of desirable microstructures and properties is dependent upon the presence of several key elements including Mn, Mo, V, Nb, Cr and Ti. Manganese, Mo and Cr act to suppress the $\gamma \rightarrow \alpha$ transformation. Niobium, V and Ti precipitates play an important role in refining the austenite grain size, as well as producing precipitation stren- gthening in the transformed material. When in solution in the austenite, these elements may also alter the transformation kinetics.

In view of the important effects of steel chemistry on microstructural development, a program was undertaken to determine how different elements may be used to alter the transformation process and the resultant steel properties. The effects of small additions of V (0 - 0.11%) and Cr (0 - 0.30%) to a typical Nb line-pipe steel were examined. Ten steels of varying Cr and V contents were controlled-rolled following a standard rolling schedule and their tensile and Charpy properties were compared. Continuous-cooling-transformation (CCT) diagrams were developed for 4 of the steels in order to ascertain ow V and Cr affect the transformation kinetics and microstructural development.

EXPERIMENTAL

The experimental steels with V content of 0 - 0.11% and Cr contents of 0 - 0.30% (Table 1) were prepared as air-induction melts. The ingots were soaked for 1-1/4 h at 1200°C and rolled to 13 mm plate using the rolling schedule given in Table 2. The temperature during rolling was monitored by a thermocouple embedded at the mid-thickness position of the plate. The plates were air cooled after rolling.

Charpy specimens were machined transverse to the rolling direction and notched in the through thickness direction of the plate. Standard Charpy tests were carried out between -120°C and 100°C to determine the impact transition curves. Two tests were performed at each temperature. Tensile samples with gauge length 25.4 mm and diameter 6.3 mm were machined in the longitudinal direction of the plate and tested at room temperature. The results reported are the average of two tests.

The microstructures of the alloys were characterized by optical examination of the plane defined by the through thickness and rolling directions. The samples were etched with a 2% nital solution.

Continuous-cooling-transformation (CCT) diagrams were determined for steels A (0 Cr, 0 V), C (0.30 Cr,0 V), G (0 Cr, 0.11 V) and I (0.31 Cr, 0.10 V) with an MMC dilatometer. The tests were performed in a vacuum or in an inert atmosphere. An austenitizing treatment of 5 min at 1150°C produced a γ grain size of $\simeq$ 60 μm in all samples. Diagrams were constructed from specimens cooled variously from 800 to 500°C in times of 3 to 3000 s. When necessary, samples were gas quenched with He; otherwise the dilatometer was programmed to simulate Newtonian cooling. The Ac_1 and Ac_3 temperatures were determined during heating at 2 K/min. After cooling, the microstructures were examined by both optical and scanning electron microscopy (SEM).

RESULTS

MICROSTRUCTURE

All the steels exhibit a banded microstructure in the as-rolled condition. In the base alloy (steel A - 0 V, 0 Cr) bands of pearlite lie parallel to the rolling plane (Fig. 1). A duplex ferrite grain size is evident with some grains as large as 25 μm, although most grains are less than 10 μm in size. The ferrite grains are equiaxed.

Addition of V produced some refinement of the ferrite grain size although a duplex structure is still evident in Steel G (0 Cr, 0.11 V), as seen in Fig. 2. There is a reduction in the extent of banding compared with Steel A and in some bands, bainite and martensite-retained austenite (M/A) appear in place of pearlite. Some ferrite grains appear to be elongated, possibly indicating that the γ - α transformation began prior to the completion of rolling.

The effects of Cr on the microstructure (Fig. 3) appear to be similar to those of V. In steel C (0.30 Cr, 0 V) there is a reduction in the ferrite grain size and in the amount of pearlite present in the microstructure as compared with Steel A. There is also evidence that the pearlite was partially replaced by lower temperature transformation products. The ferrite grains are equiaxed indicating that rolling was complete prior to the onset of the $\gamma - \alpha$ transformation.

In alloys, such as Steel I (0.31 Cr, 0.10 V), containing both Cr and V, much of the pearlite is replaced by M/A (Fig. 4). The ferrite grain size is relatively uniform and the grains are for the most part equiaxed.

PROPERTIES

The base steel (Steel A) has a yield stress of 479 MPa (69.4 ksi) and tensile strength of 537 MPa (77.8 ksi). The 20 J Charpy impact temperature is -110°C and the absorbed impact energy is 81.5 J at 20°C.

The effects of alloying additions of V and Cr to the base steel are not clearly defined (Fig. 5). In general it appears that both Cr and V additions produce small increases in the yield and tensile stresses. Vanadium is the more effective alloying agent and the tensile properties rise in proportion to the content. Little change is observed in the properties of the steels containing $\leq$ 0.15 Cr, but the effects of Cr became notable at a level of 0.30. While these general trends are apparent, there are variations within the test results that are not predicted. For example, addition of 0.055 V to the 0.15 Cr alloy produces a reduction in yield stress but addition of 0.055 V to the 0.30 Cr alloy results in an increase in yield stress. Clearly other factors play a role in determining the steel properties.

There was no detectable effect of alloy additions on the 20 J impact transition temperature. With only one exception (Steel B), the impact transition temperature lies between -100 and -110°C. The Charpy impact shelf energy varies widely from 61 J to 85 J at 20°C. As seen in Fig. 6 it correlates with the S content of the steels. The impact energy appears to be independent of either the Cr or V content.

CCT DIAGRAMS

The CCT diagrams determined for the steels A, C, G and I are shown in Figs. 7-10 respectively. Four different transformation products determined by the cooling rate are observed: polygonal ferrite, pearlite, bainite

and martensite. It should be noted that it was often difficult to determine the temperature at which martensite formation replaced the bainite transformation. As well, the formation of small amounts of pearlite at some cooling rates could not be detected by the dilatometer. In such cases, the position of the region was estimated from subsequent microscopy.

Bainite appears as a transformation product under all but the slowest ($t_{800-500°C}$ = 3000 s) cooling rates in all four steels because of the relative large ($\cong$ 60 μm) prior austenite grain size. The position of the ferrite nose appears to be unaffected by the Cr and V additions and in each case the F_s nose lies within the range of cooling rates defined by $30 < t_{800-500°C} < 60$ s.

DISCUSSION

VANADIUM

The primary goal of adding V to Nb-steels is to enhance the strength of the steels by precipitation strengthening. Most of the Nb precipitates as Nb(C,N) in the austenite prior to transformation and is thus useful for inhibiting γ-recrystallization during rolling, but contributes little to precipitation strengthening of the ferrite in the transformed steel. Vanadium carbides and nitrides have a much higher solubility in austenite than Nb(C,N) and will remain in solution until ferrite formation begins. Thus, previously observed increases in strength of 70 to 140 MPa/0.1% V) with V additions to Nb steels (1,2) are attributed to the precipitation strengthening produced by V(C,N) precipitates which form during the $\gamma - \alpha$ transformation, or in the ferrite subsequent to transformation.

In the present study increases in strength from the addition of V ($\cong$ 28 MPa/0.1% V) were smaller than those referred to above. This relatively small effect suggests that either the V has precipitated in the austenite prior to transformation, and thus is ineffective in strengthening, or that the cooling rate was sufficiently rapid that the VC precipitation in ferrite was incomplete and much of the V remained in solution. (It is to be noted that VC as opposed to VN is expected to be the strengthening agent in the present study because the N content is low ($\leq$ 0.011%) and it is likely that most of the N will be tied up in Nb(C,N) precipitates that form at high temperatures).

To test the premise that VC precipitation was incomplete, samples of steel G (0.11 V) were annealed at 650°C for times of up to one hour and the hardness determined. This treatment should cause the precipitation of any excess V in solution. As seen from Table 3 the increases in hardness were very small, indicating there had been little further V precipitation. This suggests that the small degree of precipitation strengthening obtained in the as-rolled condition was a consequence of the large amount of V precipitation in the austenite prior to transformation, rather than incomplete precipitation subsequent to transformation. In support of this conclusion, a recent study suggests that strain-induced precipitation of VC occurs in the austenite following deformation in the range of 830-850°C (3). It is apparent that the rolling schedule used in the present study (79% reduction below 900°C, i.e., below the γ-recrystallization temperature in Nb-steels) produced a large amount of VC precipitation in the deformed austenite thereby depleting the amount of V available for precipitation strengthening of the ferrite. Davenport et al. (4) have shown that a greater precipitation strengthening effect is obtained with a finishing temperature of 900°C as opposed to 815°C. It thus appears that a higher tensile strength could have been obtained in the present study if rolling had been completed at higher temperature (4).

It has been reported that the presence of V in austenite prior to transformation promotes the formation of polygonal ferrite, shifting the ferrite start temperature upwards and moving the ferrite nose to shorter times in CCT diagrams. Cochrane and Morrison (5) observed these effects of V in Nb-steels of similar composition to those used in the present study. However, their results stand in marked contrast to the findings presented here in which the addition of 0.11 V had virtually no effect on the CCT diagram. It is noted that in the work of Cochrane and Morrison there is a large difference in grain size between the Nb-steel (190 μm) and the Nb-V steel (130 μm), a factor which would increase the transformation rate in the Nb-V steel and thus exaggerate the effect of the V addition. On the other hand, in the present study the Nb-V steel (Steel G) had a higher Mn content (1.62 versus 1.46 wt %) than the Nb steel (Steel A). Because Mn acts to suppress ferrite formation, this difference in composition will tend to mask the effects of V in promoting ferrite formation. Clearly, more work is required to ascertain the role of V in ferrite formation.

Vanadium also acts to suppress pearlite formation, thereby allowing

the formation of lower temperature transformation products in the high C austenite which remains after ferrite transformation (5,6). This behaviour is evident in Fig. 11 where the fraction of steel transformed is plotted against temperature for a cooling time of $t_{800-500°C}$ = 1000 s. While the ferrite transformation begins at slightly higher temperature in Steel G (0.11 V) and proceeds at approximately the same rate as Steel A over much of the temperature range, below 620°C there is an increasing divergence between the two curves as the transformation rate of Steel G is markedly retarded. Pearlite begins to form below 620°C at this cooling rate. Comparing the final microstructures after cooling (Figs. 12a and 12b) it is clear that pearlite formation in Steel G has been suppressed which results in a larger volume fraction of bainite in Steel G than in Steel A.

CHROMIUM

The results determined here for the effects of Cr additions on the properties of low-alloy steels are similar to other results reported in the literature. Wiedenoff et al. (7) examined the effects of Mo and Mo + Cr additions to the properties of steels and found little change in yield strength or the fracture transition temperature until the total Mo + Cr content exceeded 0.25%. In the present study, steels with 0.3% Cr content had improved yield and tensile strength while steels with lower Cr contents showed little change.

The small effect of Cr additions observed here is related to the effects of Cr on transformation kinetics. Whereas it is generally accepted that Cr acts like Mo to displace the ferrite and pearlite regions to longer times in CCT diagrams and to lower the $\gamma - \alpha$ transformation temperature, Cr appears to have a much weaker effect than Mo (8). In the CCT diagram shown in Fig. 8 the effect of Cr on the F_s temperature when compared with the base metal, is negligible. Although the CCT diagrams have been developed for undeformed coarse-grained austenite which presents a far different structure prior to transformation than the fine pancaked austenite grains found in controlled-rolled steels, it is likely, nonetheless, that the results will provide an indication of the effects of alloy element additions. The unchanged CCT diagram is consistent with the small effect of Cr on the Ar_3 temperature reported by Ouchi et al. in controlled-rolled steels where Ar_3 was given by:

$$Ar_3\ (°C) = 910 - 310C - 80Mn - 20Cu - 15Cr - 55Ni - 80Mo \qquad (1)$$

The alloying elements are in wt % (8). According to this equation, an addition of 0.30 Cr would reduce Ar_3 by only 4.5°C, a change unlikely to produce the structural changes required to significantly alter the properties of the steel. Clearly the addition of 0.3% Cr has little effect and much larger additions are required to alter the transformation behaviour and, consequently, the structure and properties of these steels.

VANADIUM + CHROMIUM

Although there was considerable variation in the observed yield strengths, in general, it appeared that the effects of Cr and V on strength were additive and there was no evidence of any synergistic effect. It has been asserted that the presence of Cr in V-bearing steels would lower the transformation temperature leading to refinement of the precipitate size and distribution, thereby enhancing the material strength (10). However, as discussed, the rolling schedule used in this work did not produce optimal conditions for V precipitation in the ferrite and, therefore, this effect was not studied in detail. It would seem that the very small effect of Cr on the transformation temperature should not produce any significant effect on precipitation behaviour.

For the most part the CCT diagram for Steel I (0.31 Cr, 0.10 V) is similar to that of the other compositions. However, it is apparent that the presence of Cr + V has a strong effect in suppressing the transformation of the carbon-rich austenite during the final stages of transformation. Figure 11 shows that (for a cooling time $t_{800-500}$ = 1000 s) below 620°C the transformation is strongly retarded. The transformed microstructure (Fig. 12c) contains very little pearlite and a considerable fraction of bainite. This retardation effect is surprisingly large considering that Steel C, containing only 0.30 Cr, produced a small retardation effect compared with Steel A, only in the very last stages of transformation.

SULFUR

The deleterious effects of sulfur on the Charpy shelf energy, as seen in Fig. 6, are well known (11,12). In the ductile fracture process, sulfide inclusions act as sites for the nucleation of voids which grow and coalesce, leading to final fracture. The strong dependence of the shelf

energy on the sulfur content clearly indicates the need for careful control of sulfur content together with the potential value of controlling the shape of sulfide inclusions.

CONCLUSIONS

Additions of V and/or Cr to a controlled rolled Nb-steel had little effect on the microstructure; they produced a slight refinement of grain size and reduced the pearlite content. The V additions produced increases in yield and tensile strengths of approximately 28 MPa/0.1% V (4 ksi/0.1% V). Alloys containing 0.30 Cr exhibited slightly increased yield and tensile strengths, but smaller additions had little effect on the properties of the steel. Neither the Cr nor V additions affected the 20 J Charpy transition temperature.

The Charpy shelf energy at 20°C was determined solely by the S content of the steel and was not affected by either the V or Cr content.

The additions of Cr and/or V had very little effect on the transformation kinetics as evidenced by the CCT diagrams. Vanadium did appear to be effective in inhibiting pearlite formation and the presence of V + Cr had a very strong retarding effect in the final stages of transformation.

ACKNOWLEDGEMENT

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Table 1 - Alloy composition

Steel	Cr	V	C	Mn	Nb	S	P	Si	Al	N
A	-	-	0.11	1.46	0.055	0.002	<0.002	0.28	0.02	0.0069
B	0.16	-	0.10	1.45	0.055	0.003	0.002	0.26	0.025	N.D.
C	0.30	-	0.10	1.47	0.05	0.002	0.002	0.24	0.025	N.D.
D	-	0.055	0.11	1.45	0.055	0.007	0.002	0.27	0.025	0.011
E	0.15	0.055	0.11	1.44	0.055	0.007	0.002	0.26	0.027	0.012
F	0.30	0.06	0.10	1.43	0.05	0.002	0.002	0.22	0.015	0.011
G	-	0.11	0.095	1.62	0.055	0.005	<0.002	0.295	0.05	0.0058
H	0.16	0.11	0.10	1.51	0.065	0.005	<0.002	0.295	0.02	0.0046
I	0.31	0.10	0.105	1.50	0.055	0.002	<0.002	0.275	0.075	0.0086
J	0.195	0.08	0.105	1.50	0.05	0.002	<0.002	0.275	0.055	N.D.

N.D. - Not Determined

Table 2 - Rolling schedule

Pass No.	Mill setting (mm)	Temperature (°C)
1	117.0	1150
2	104.0	1125
3	94.0	1100
4	84.0	1075
5	74.5	1050
6	63.5	1025
7	56.0	900
8	48.0	890
9	42.0	880
10	35.5	865
11	30.5	850
12	25.5	835
13	21.5	825
14	18.0	815
15	14.0	805
16	11.5	790

Table 3 - Hardness after isothermal annealing at 650°C - Steel G (0.11 V)

Annealing time (min)	Hardness
0	189.5
15	189.0
30	189.0
60	191.5

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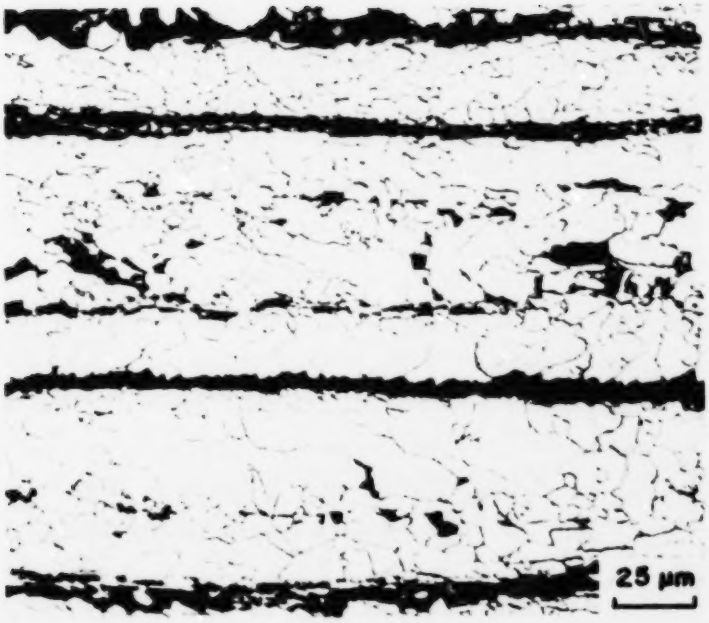


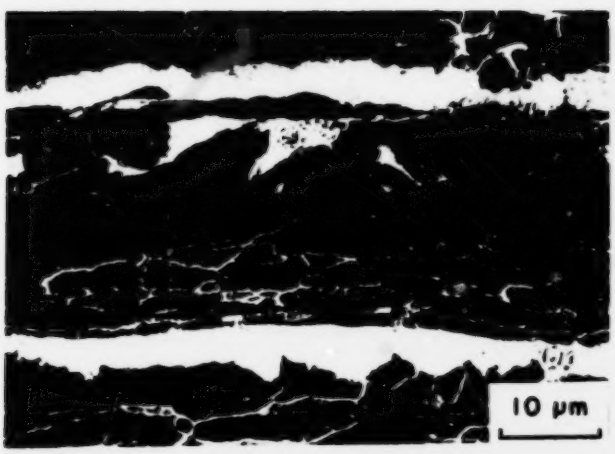


Fig. 1. Microstructures of Steel A (0 V, 0 Cr)
(a) optical micrograph.
(b) SEM micrograph showing pearlite structure of bands.
(neg 8263)

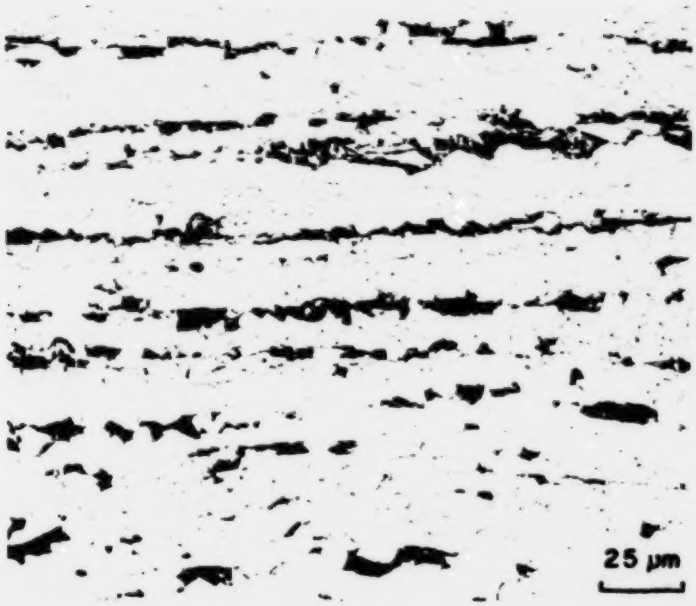


Fig. 2: Microstructure of Steel G (0 Cr, 0.11 V).

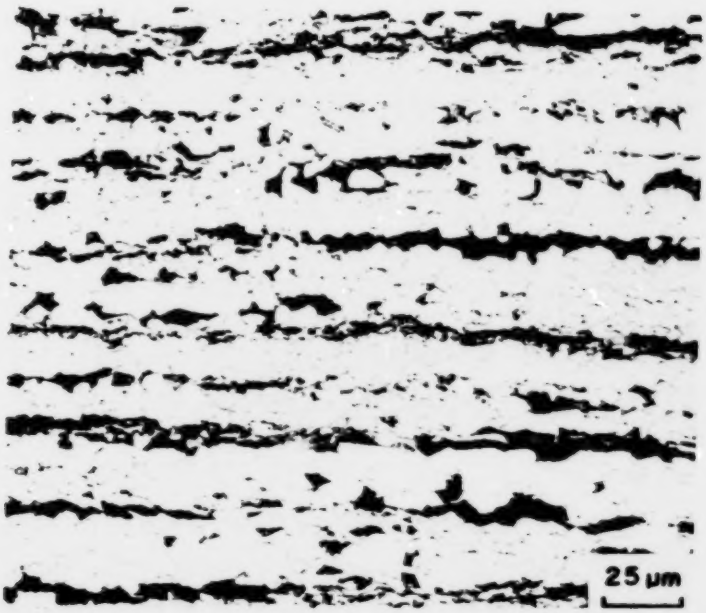
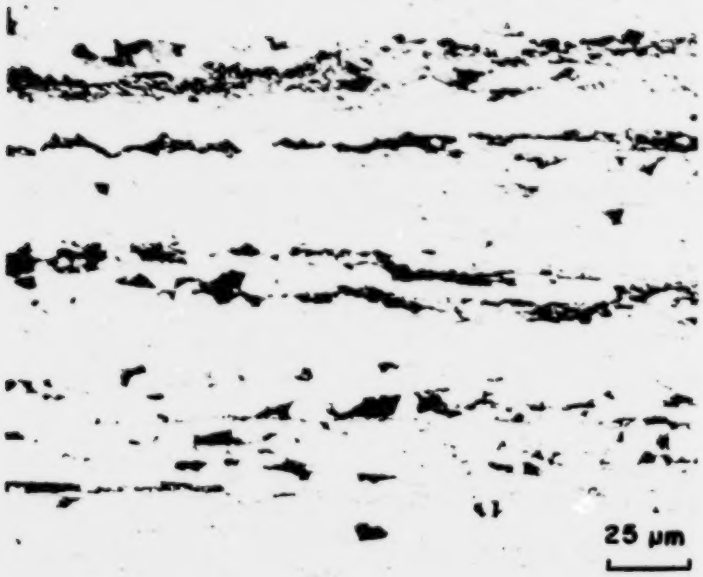


Fig. 3: Microstructure of Steel C (0.30 Cr, 0 V).



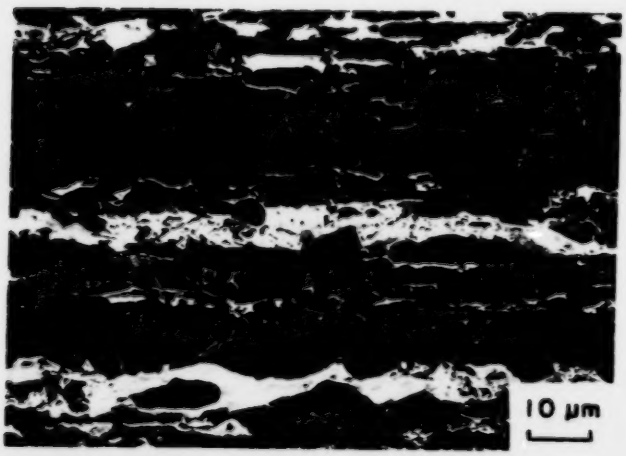
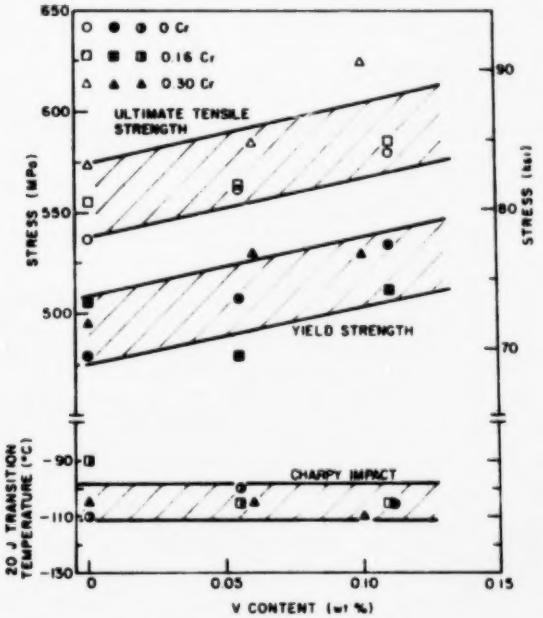
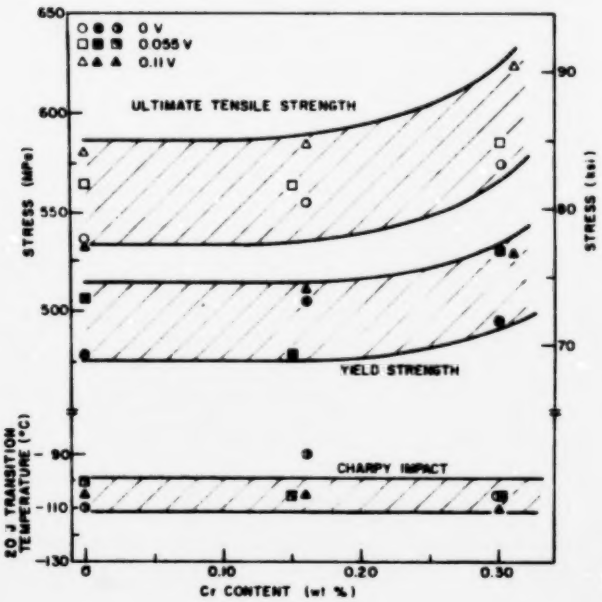


Fig. 4: Microstructures of Steel I (0. 31 Cr, 0.10 V)
(a) optical micrograph.
(b) SEM micrograph showing M/A structure in the bands.
(neg. 8264)



(a) V content (neg. 8259)



(b) (neg.8256)

Fig. 5: Variation of mechanical properties of the as-rolled plate with Cr content.

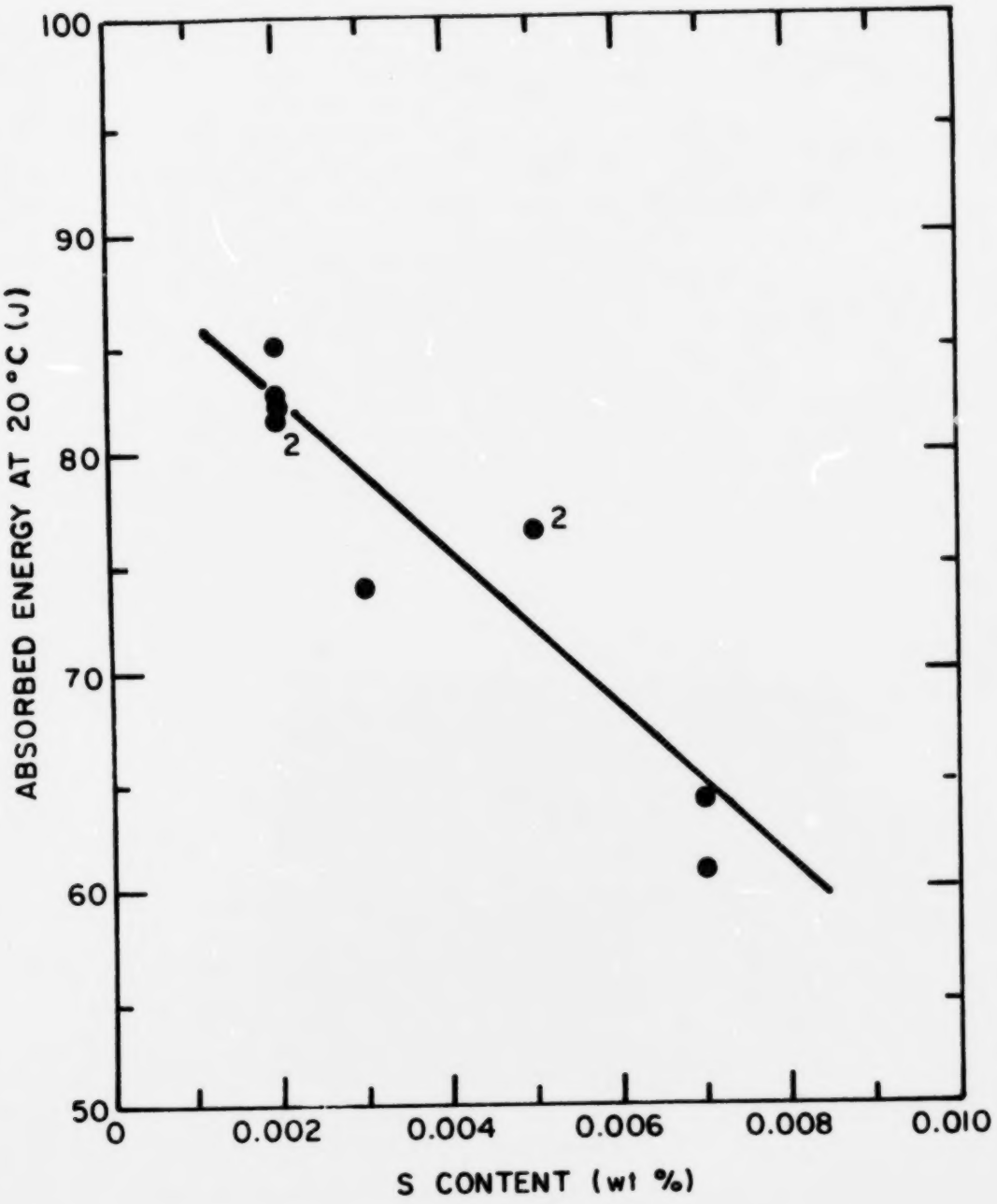


Fig. 6: Dependence of the Charpy shelf energy at 20°C on S content. (neg. 8255)

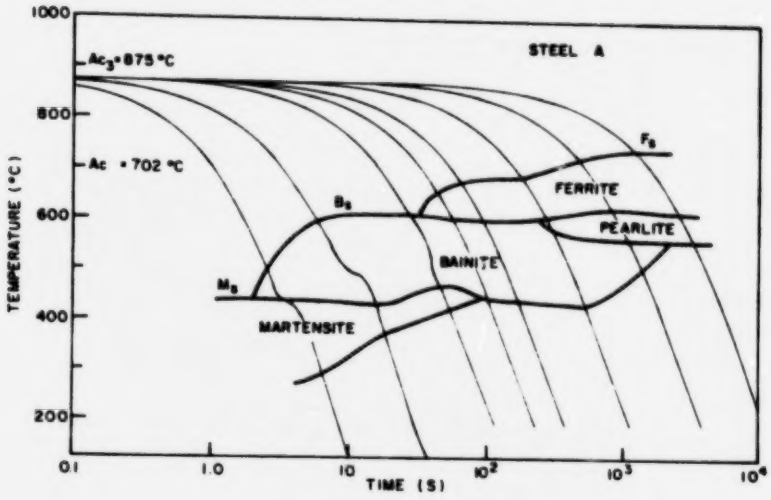


Fig. 7: CCT diagram for steel A. (neg. 8262)

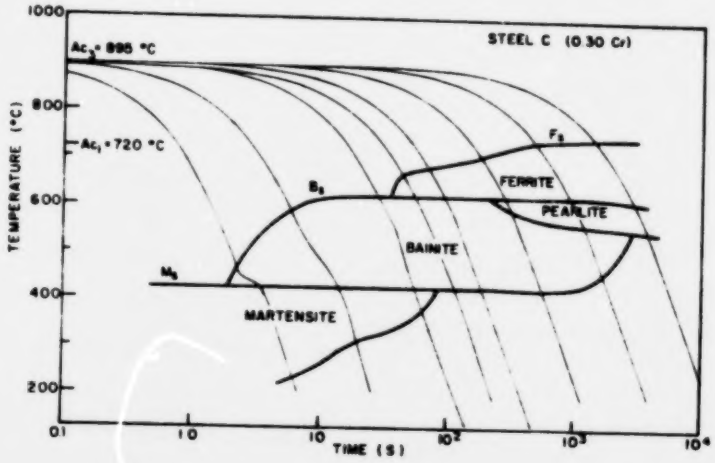


Fig. 8: CCT diagram for steel C. (neg. 8606)

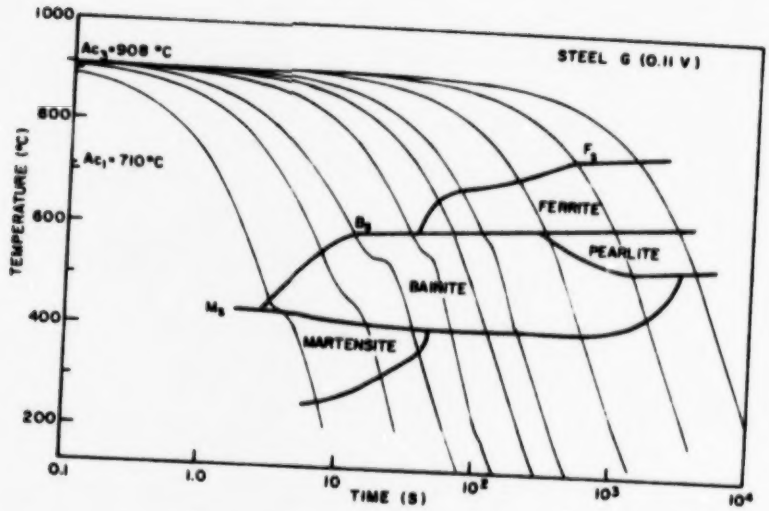


Fig. 9: CCT diagram for steel G. (neg. 8258)

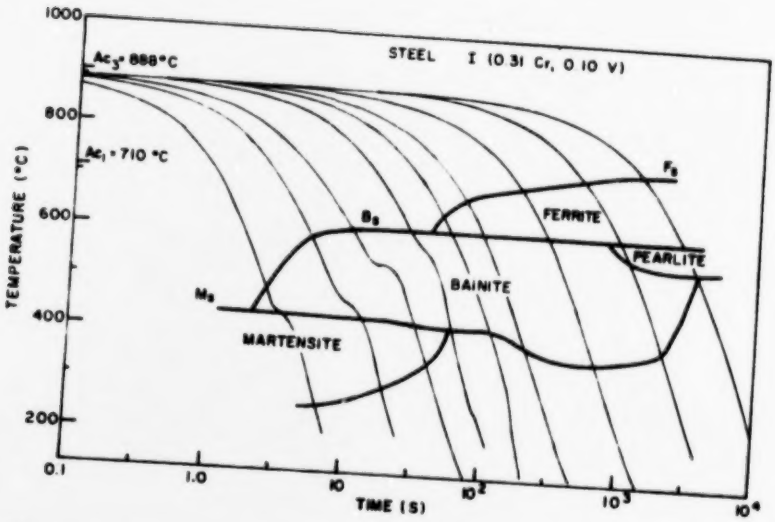


Fig. 10: CCT diagram for Steel I. (neg. 8261)

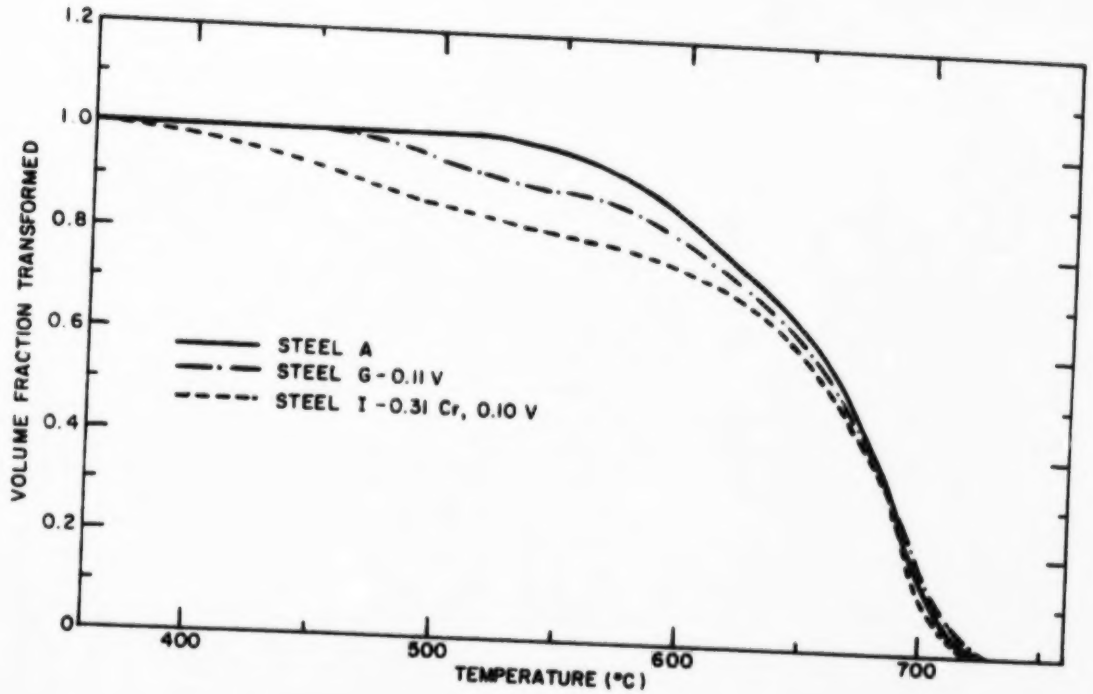
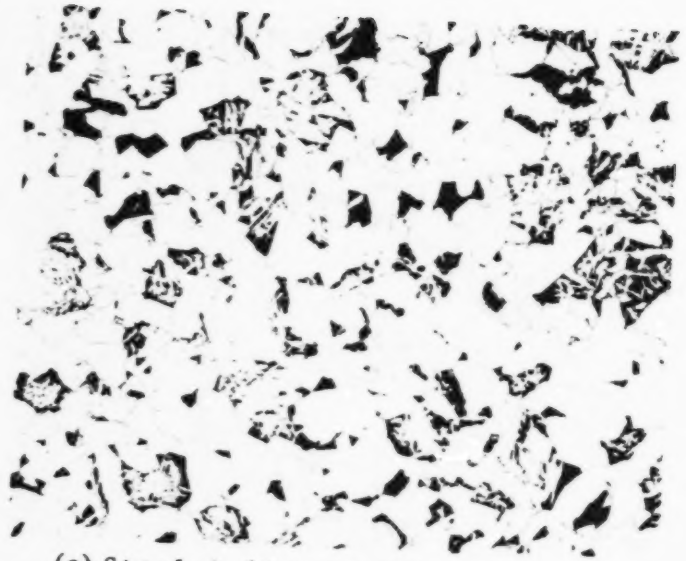
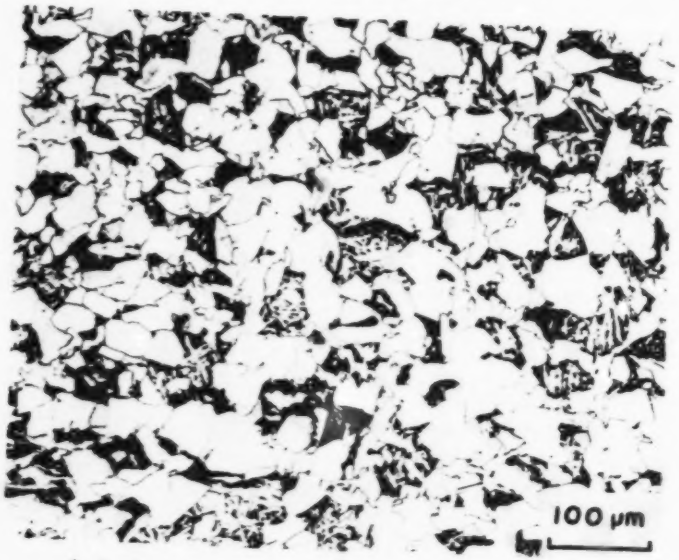


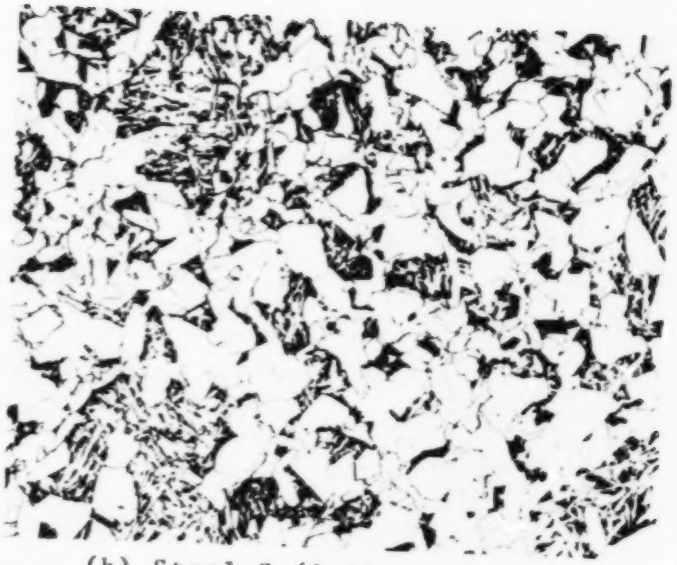
Fig. 11: Comparison of the transformation temperature dependence of steels A, G, and I at cooling time $t_{800-500°C}$ = 1000 s. (neg. 8257)



(a) Steel A (0 V, 0 Cr).



(c) Steel I (0.10 V, 0.31 Cr).



(b) Steel G (0.11 V, 0 Cr).

Fig. 12. Comparison of microstructures after dilatometer treatment, ($T_{800\text{-}500°C}$ = 1000 s).